

Polyester, Production Method Thereof, Fibers Therefrom,  
and Catalyst for Polymerization of Polyester

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Field of the Invention

The present invention relates to a polyester having improved fiber formability. More specifically, the present invention relates to a polyester produced 10 by using an antimony catalyst of specific composition and a production method thereof. The polyester has a controlled crystallization rate, undergoes few fiber breakages during high-speed spinning and has excellent stretchability and twistability and good color. 15 Further, the present invention also relates to fibers comprising the polyester. The present invention also relates to a catalyst for polymerization of the polyester.

Description of the Related Art

20 A polyester typified by a polyethylene terephthalate is a material having high strength, a high Young's modulus and excellent thermal dimensional stability. Fibers formed from the polyester are used in a wide variety of applications such as clothing and 25 industrial materials. In addition, recently, use of high-speed spinning has simplified conventionally required stretching and heat treatment steps into one step, making it possible to decrease costs. Thus, significance thereof has been further increasing.

30 However, when high-speed spinning is carried out, the polyester has the following problem in spite of the above excellent properties. That is, the polyester has a quality-related problem that crystallization of the polyester at the time of stretching and processing

fibers must be controlled in producing the polyester fibers and an increase in spinning speed makes orientation and crystallization remarkable, resulting in significant deterioration in the shrinkage of the 5 fibers. Further, it also has a problem that the number of fiber breakages during high-speed spinning is liable to increase. The problem of fiber breakages is particularly important, because a production step using high-speed spinning is subjected to a greater influence 10 of the fiber breakages than a conventional production step using low-speed spinning. That is, fiber breakages are liable to spread to adjacent fibers, and it takes a large amount of time to recover a weight having undergone a fiber breakage by resetting a fiber 15 on the weight, thereby making deterioration in productivity due to the fiber breakages significant.

Therefore, in high-speed spinning, it is essential that the frequency of occurrence of fiber breakages be less than before, so as to secure operation 20 stability.

To solve the problem, a variety of proposals have been made on improvements to spinning conditions such as a spinning temperature and cooling conditions and the structures of a spinneret and a heating pipe under 25 the spinneret. However, these measures have limitations and cannot decrease the number of fiber breakages significantly.

Further, attempts to solve the problem by modification of the polyester have also been made. For 30 example, production of polyester having controlled molecular weight distribution has been attempted by paying attention to a Z average molecular weight, a weight average molecular weight and a number average molecular weight (refer to Patent Publication 1).

However, at the time of spinning, the molecular weight distribution is shifted to an equilibrium state due to an ester redistribution reaction. That is, control of the redistribution reaction by a terminal blocking agent or the like is required for making molecular weight distribution after fiber production monodisperse. This is difficult from an industrial standpoint.

Further, a technique for controlling orientation of the polyester by adding a vinyl polymer which contains a modifying component having a low molecular weight such as 1,200 or 3,000 to the polyester to allow the vinyl polymer to react with the polyester so as to form "molecular crosslinking" is disclosed (refer to Patent Publication 2). The technique is a technique using the low-molecular-weight vinyl polymer as a molecular polyvalent crosslinking agent. However, the technique has a problem that since ester forming reactive groups existing in side chains of the vinyl polymer have an excessively short distance between the reactive groups (distance between branch points), the polymer is liable to produce gel in a polymerization reactor or spinning machine and forms foreign matter, thereby degrading fiber formability.

Meanwhile, as means for controlling orientation and crystallization of the polyester, a method comprising adding a polyether (polyalkylene glycol) or isophthalic acid to the polyester and copolymerizing them is also known (Refer to Patent Publications 3 and 4). That is, a technique comprising adding the low-molecular-weight polyether to the polyester, copolymerizing them and performing melt-spinning at a high take-up speed is disclosed. The technique described in the publication has a problem that although

"crystallization" of polyester fibers melt-spun at a take-up speed of 2,000 m/min or higher is controlled, the strength of the fibers lowers.

Meanwhile, polyesters containing at least one sodium compound selected from the group consisting of sodium hydroxide, sodium carbonate, sodium benzoate and sodium stearate and polyesters containing trimellitic acid and a Ca salt and/or Ba salt of trimellitic acid are proposed. These polyesters are effective for control of fiber breakages to a certain extent (refer to Patent Publications 5 and 6). However, these polyesters have limitations on improvement of the melt extrudability of the polymers to improve a spinning speed and a production capacity. That is, when a spinning temperature is increased to improve the melt extrusion capability of the polymers, alkalinolysis may occur due to an alkali metal salt or alkaline earth metal salt or pack blocking may occur due to agglomeration of fine particles, thereby limiting continuous running time.

As described above, it is a current situation that prevention of fiber breakages in high-speed spinning is not achieved yet by modification of the polymer by the prior art.

25 (Patent Publication 1) JP-A 2001-89935 (the term "JP-A" as used herein means an "unexamined published Japanese patent application")

(Patent Publication 2) JP-A 11-61568

(Patent Publication 3) JP-A 11-240944

30 (Patent Publication 4) JP-A 2001-271226

(Patent Publication 5) JP-A 11-279836

(Patent Publication 6) JP-A 11-247024

#### SUMMARY OF THE INVENTION

## (Problems to be solved by the Invention)

A first object of the present invention is to provide a polyester with a controlled crystallization rate which forms fibers stably even in high-speed spinning and a production method thereof. A second object of the present invention is to provide fibers comprising the polyester and having a controlled crystallization rate. A third object of the present invention is to provide a catalyst for polymerization 10 of the polyester.

## (Means for solving the Problems)

The present inventors have made intensive studies to solve the above problems. As a result, they have found that when a specific antimony catalyst is used, 15 a polyester which has an improved crystallization rate, can endure high-speed spinning over a long time and has good color can be obtained. The present invention has been completed by this finding.

That is, the present invention is a polyester 20 obtainable in the presence of an antimony catalyst, wherein the antimony catalyst comprises:

- (i) diantimony trioxide, and
- (ii) 1 to 10 wt% of diantimony tetraoxide and/or diantimony pentaoxide based on diantimony trioxide.

25 Further, the present invention is fibers obtained by melt-spinning the above polyester.

Further, the present invention is a method for producing a polyester by subjecting a dicarboxylic acid or an ester forming derivative thereof and a diol or 30 an ester forming derivative thereof to an esterification reaction or a transesterification reaction and then carrying out a polycondensation reaction in the presence of an antimony catalyst, wherein the antimony catalyst comprises:

- (i) diantimony trioxide, and
- (ii) 1 to 10 wt% of diantimony tetraoxide and/or diantimony pentaoxide based on diantimony trioxide.

Further, the present invention is a catalyst for 5 polymerization of polyester, the catalyst comprising:

- (i) diantimony trioxide, and
- (ii) 1 to 10 wt% of diantimony tetraoxide and/or diantimony pentaoxide based on diantimony trioxide.

#### Effects of the invention

10 According to the present invention, a polyester having a controlled crystallization rate, a reduced number of fiber breakages during spinning, excellent stretchability and twistability and good color and fibers of the polyester can be obtained.

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#### Best Mode for the Embodiments of the Invention (Polyester)

The polyester of the present invention is a linear saturated polyester having recurring units comprising 20 a dicarboxylic acid or an ester forming derivative thereof and a diol or an ester forming derivative thereof.

Illustrative of the dicarboxylic acid or ester forming derivative thereof include terephthalic acid, 25 isophthalic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, 1,4-cyclohexyldicarboxylic acid, P-hydroxybenzoic acid, dimethyl terephthalate, dimethyl isophthalate, dimethyl 2,6-naphthalenedicarboxylate, dimethyl 30 2,7-naphthalenedicarboxylate, dimethyl 1,4-cyclohexyldicarboxylate, and diphenyl esters and acid halides of other dicarboxylic acids. Terephthalic acid, 2,6-naphthalenedicarboxylic acid and their ester forming derivatives are preferred. The

amount of these main dicarboxylic acid components is preferably 70 mol% or higher, more preferably 80 mol% or higher, much more preferably 90 mol% or higher, based on all dicarboxylic acid components.

5       Illustrative examples of the diol or ester forming derivative thereof include ethylene glycol, 1,3-propanediol, 1,2-propanediol, 1,4-butanediol, diethylene glycol, 1,6-hexanediol and 1,4-cyclohexane dimethanol. Ethylene glycol and 1,4-butanediol are 10 preferred. The amount of these main diol components is preferably 70 mol% or higher, more preferably 80 mol% or higher, much more preferably 90 mol% or higher, based on all diol components.

More preferred is a polyethylene terephthalate 15 comprising, as a main constituent, an ethylene terephthalate unit using terephthalic acid or an ester forming derivative thereof as the dicarboxylic component and ethylene glycol as the diol component. The main constituent constitutes 60 mol% of all 20 recurring units. The amount of the ethylene terephthalate unit is preferably 70 mol% or higher, more preferably 80 mol% or higher, much more preferably 90 mol% or higher, based on all recurring units.

Further, the polyester of the present invention 25 may be copolymerized with other components in amounts that do not impair the physical properties of the polyester as a general-purpose resin. Illustrative examples of the components copolymerizable with the polyester include dicarboxylic acids or ester forming 30 derivatives thereof and diols or ester forming derivatives thereof other than those mentioned above.

Illustrative examples of dicarboxylic acid components copolymerizable with the polyester of the present invention include terephthalic acid,

2,6-naphthalenedicarboxylic acid, isophthalic acid, 1,4-cyclohexyldicarboxylic acid, adipic acid, sebacic acid, phthalic acid, phthalic anhydride, 5-sodium sulfoisophthalate, 5-tetrabutyl phosphonium

5 sulfoisophthalate, P-hydroxybenzoic acid, dimethyl terephthalate, dimethyl 2,6-naphthalenedicarboxylate, dimethyl isophthalate, dimethyl 1,4-cyclohexyldicarboxylate, dimethyl adipate, dimethyl sebacate, dimethyl phthalate, dimethyl

10 5-sodium sulfoisophthalate, and dimethyl 5-tetrabutyl phosphonium sulfoisophthalate. Particularly preferred are terephthalic acid, 2,6-naphthalenedicarboxylic acid, dimethyl terephthalate and dimethyl

15 2,6-naphthalenedicarboxylate. The amount of the copolymerizable dicarboxylic acid component is preferably 30 mol% or lower, more preferably 20 mol% or lower, much more preferably 10 mol% or lower, based on all dicarboxylic acid components.

20 Further, illustrative examples of diol components copolymerizable with the polyester of the present invention include ethylene glycol, 1,4-butanediol, diethylene glycol, propylene glycol, 2,2-dimethyl-1,3-propanediol, dipropylene glycol,

25 1,6-hexanediol, 1,4-hexane dimethanol, dimethylol propionate, a poly(ethylene oxide)glycol and a poly(tetramethylene oxide)glycol. The amount of the copolymerizable diol component is preferably 30 mol% or lower, more preferably 20 mol% or lower, much more preferably 10 mol% or lower, based on all diol components.

These dicarboxylic acids or ester forming derivatives thereof and diols or ester forming derivatives thereof may be used alone or in combination

of two or more.

Further, the polyester of the present invention may be copolymerized with a polycarboxylic acid such as trimellitic acid, trimesic acid, trimellitic anhydride, pyromellitic acid or monopotassium trimellitate or a polyhydroxy compound such as glycerine, sodium dimethylol ethyl sulfonate or potassium dimethylol propionate in such an amount that does not impair the object of the present invention.

The polyester of the present invention preferably comprises a polyethylene terephthalate as a main constituent and satisfies (A) to (D) simultaneously. As the (A), the amount of copolymerized diethylene glycol is preferably 0.6 to 1.4 wt% based on the total weight of the polyester. When the amount of diethylene glycol copolymerized is too small, viscosity at the time of melt-spinning becomes too high, resulting in poor spinnability at the time of high-speed spinning. When the amount of diethylene glycol copolymerized is too large, heat resistance becomes poor, so that sublimed foreign matter is liable to be produced in a spinneret. To have the amount of diethylene glycol copolymerized within a given range, the following methods can be used, for example. For instance, to increase the copolymerized amount, a method of adding diethylene glycol in a required amount may be employed. Meanwhile, to decrease the copolymerized amount, there can be employed a method of reducing the amount of by-produced diethylene glycol by making smaller the molar ratio between the diol or ester forming derivative thereof and the dicarboxylic acid or ester forming derivative thereof as raw materials, a method of decreasing pre-reaction heating retention time under reduced pressure in the polycondensation reaction or a method

of reducing the polycondensation reaction temperature.

As the (B), the cooling crystallization temperature ( $T_{cd}$ ) of the polyester of the present invention is preferably 180 to 205°C, more preferably 5 185 to 200°C. When  $T_{cd}$  is too high, crystallization starts right underneath the spinneret immediately after spinning, and the fiber structure is fixed, thereby causing poor stretchability and processability. When  $T_{cd}$  is too low, crystallization starts after 10 orientation of the polyester proceeds after spinning, orientation crystallization becomes dominant, so that a spinning condition may deteriorate or stretchability and processability may become poor.

As the (C), the difference between the heating 15 crystallization temperature ( $T_{ci}$ ) and cooling crystallization temperature ( $T_{cd}$ ) of the polyester of the present invention, i.e.,  $T_{cd} - T_{ci}$ , is preferably 5 to 30°C, more preferably 15 to 25°C. When  $T_{cd} - T_{ci}$  is large, crystallization in fiber production proceeds 20 excessively, so that stretchability deteriorates and fiber breakages during spinning and/or stretching, lapping, non-uniform stretching and the like are liable to occur. When  $T_{cd} - T_{ci}$  is small, the spun polyester does not crystallize easily and the fiber structure is 25 not formed, resulting in insufficient fiber strength.

A polyester having  $T_{cd}$  and  $T_{cd} - T_{ci}$  within the above ranges can be produced by using the antimony catalyst of the present invention and controlling the amount of diethylene glycol copolymerized to 0.6 to 1.4 30 wt% based on the total weight of the polyester as described above.

As the (D), the half-time of crystallization  $\tau$  at 200°C of the polyester of the present invention is preferably 60 to 90 seconds, more preferably 65 to 80

seconds. When  $\tau$  is too short, the crystallization rate is so high that the fiber structure is fixed rapidly. Hence, sufficient relaxation time cannot be secured, stretchability becomes poor, and fiber breakages during 5 spinning and/or stretching, stretch lapping or non-uniform stretching is liable to occur. Meanwhile, when  $\tau$  is too long, crystallization proceeds too slowly, a crystal structure is not formed, resulting in poor fiber strength. A polyester having 10 semicrystallization time within the above range can be produced by using the antimony catalyst of the present invention and controlling the amount of diethylene glycol copolymerized to 0.6 to 1.4 wt% based on the total weight of the polyester as described above.

15 The content of an antimony compound in the polyester of the present invention is preferably 0.01 to 0.1 wt%, more preferably 0.02 to 0.08 wt%.

The polyester of the present invention may contain additives which are generally used in producing a 20 polyester, e.g., a metal compound catalyst containing a metal element such as lithium, sodium, calcium, magnesium, manganese, zinc, antimony, germanium or titanium, a phosphorus compound as a coloration inhibitor, and inert particles and an organic compound 25 which are used for other modification of the polyester in such an amount that does not impair the object of the present invention.

(Antimony Catalyst)

The antimony catalyst of the present invention 30 comprises:

- (i) diantimony trioxide, and
- (ii) 1 to 10 wt% of diantimony tetraoxide and/or diantimony pentaoxide based on diantimony trioxide.

When the content of diantimony tetraoxide and/or

diantimony pentaoxide is lower than 1 wt% based on diantimony trioxide, the catalyst shows a poor crystallinity controlling effect, while when the content is higher than 10 wt%, the catalyst has 5 insufficient catalytic activity, so that the polyester polycondensation reaction proceeds very slowly disadvantageously. The content of diantimony tetraoxide and/or diantimony pentaoxide is preferably 1 to 8 wt%, more preferably 1 to 5 wt%, based on 10 diantimony trioxide.

Either or both of diantimony tetraoxide and diantimony pentaoxide may be contained. When both of them are contained, their ratio may vary within a given range.

15 The antimony catalyst of the present invention can be obtained by mixing diantimony tetraoxide and/or diantimony pentaoxide into diantimony trioxide as appropriate.

Why the crystallization rate of the polyester can 20 be controlled by the antimony catalyst of the present invention is not quite known. However, according to the experiment conducted by the present inventor, the crystallization rate of the polyester could be controlled by the present antimony catalyst obtained 25 by adding diantimony tetraoxide and/or diantimony pentaoxide to diantimony trioxide.

In the antimony catalyst of the present invention, (a) the content of a Pb (lead) element is preferably 1 to 100 ppm. The content of the Pb element is more 30 preferably 1 to 80 ppm. When the content of the Pb element is high, the catalyst exhibits a poor crystallinity controlling effect and shows poor color. Reducing the content of the Pb element to lower than 1 ppm involves difficult crystallization

(purification) and high costs and lacks industrial significance.

Further, in the antimony catalyst of the present invention, (b) the content of an As (arsenic) element is preferably 1 to 100 ppm. The content of the As element is more preferably 1 to 80 ppm. When the content of the As element is high, the catalyst exhibits a weak crystallinity controlling effect. Reducing the content of the As element to lower than 1 ppm involves difficult crystallization (purification) of antimony and high costs and lacks industrial significance.

Further, in the antimony catalyst of the present invention, (c) an Fe element is preferably substantially not contained. When the Fe element is contained, the color of the polyester deteriorates. "Substantially not contained" indicates being undetectable by a general analyzing technique at the time of application.

By reducing the contents of these metal elements which are impurities in the antimony catalyst to predetermined contents lower than conventional contents, the amount of a material which serves a crystal nucleus when the polyester crystallizes can be controlled. It is conceived that the crystallization rate of the polyester can be controlled as a result of that.

Accordingly, in diantimony trioxide constituting the antimony catalyst of the present invention, (a) the content of the Pb element is preferably 1 to 100 ppm, more preferably 1 to 80 ppm. Further, (b) the content of the As element is preferably 1 to 100 ppm, more preferably 1 to 80 ppm. In addition, (c) the Fe element is preferably substantially not contained.

Further, in diantimony tetraoxide and/or

diantimony pentaoxide constituting the antimony catalyst of the present invention, (a) the content of the Pb element is preferably 1 to 100 ppm, more preferably 1 to 80 ppm. Further, (b) the content of the As element is preferably 1 to 100 ppm, more preferably 1 to 80 ppm. In addition, (c) the Fe element is preferably substantially not contained.

Antimonies having low contents of Pb, As and Fe can be produced by purifying diantimony trioxide, diantimony tetraoxide or diantimony pentaoxide by crystallization. The crystallization process comprises melting, oxidation and cooling steps. For example, in the case of diantimony trioxide, diantimony trioxide is molten, and the content of Pb in the molten liquid phase can be determined by the melting temperature. Further, by adjusting the quantity of air to be fed in an oxidation tank, Pb whose vapor pressure is higher than diantimony trioxide can be removed selectively. Then, by filtering the resulting product by use of a filter having predetermined openings when it is sent to a cooling tank, the contents of As and Fe can be controlled. Thereafter, by controlling the cooling rate and the cooling temperature, the amount of As taken into diantimony trioxide crystals can be controlled.

(Production Method of Polyester)

The polyester of the present invention can be produced by subjecting the above dicarboxylic acid or ester forming derivative thereof and the above diol or ester forming derivative thereof to an esterification reaction or a transesterification reaction and then carrying out a polycondensation reaction in the presence of the above antimony catalyst. In this case, copolymerizable components as described above may be

used.

The polyester to be obtained is produced by using the antimony catalyst in an amount of preferably 0.01 to 0.1 wt%, more preferably 0.02 to 0.08 wt%, based on 5 the weight of the polyester. When the amount of the antimony catalyst is small, the polycondensation reaction does not proceed to a sufficient extent at the time of production of the polyester, so that a polyester having satisfactory mechanical characteristics cannot 10 be obtained. When the amount of the antimony catalyst is large, depolymerization proceeds during fiber production, and the intrinsic viscosity of the polyester lowers, whereby the strength and color of the polyester may deteriorate.

15 For example, first of all, a first-stage transesterification reaction or esterification reaction is conducted to produce a diol ester of terephthalic acid and/or a lower polymer thereof, in which a dicarboxylic acid and the diol are directly 20 subjected to an esterification reaction, a lower alkyl ester of terephthalic acid such as dimethyl terephthalate and the diol are subjected to a transesterification reaction, or a terephthalic acid is reacted with an oxide. When the dicarboxylic acid 25 and the diol are directly esterified, the polyester can be produced by charging slurry whose molar ratio between the diol and the dicarboxylic acid is adjusted to 1.1 to 2.0 into a reactor equipped with a stirring blade and a distilling column and distilling out a given 30 amount of water at normal pressure or a gauge pressure of 0.3 MPa or lower at 230 to 270°C. When the dicarboxylic acid ester and the diol are transesterified, the transesterification reaction can be carried out in the presence of a transesterification

catalyst at a molar ratio of diol/dicarboxylic acid ester of 1.4 to 2.0 at normal pressure or a gauge pressure of 0.3 MPa or lower with the temperature being increased from room temperature until a given amount 5 of an alcohol is distilled out.

Then, the obtained product is fed into a polymerization reactor equipped with a stirring blade, a cooling device and vacuum equipment, and the polyester can be produced by a second-stage polycondensation 10 reaction in which a polycondensation reaction is carried out until a desired polymerization degree is achieved with stirring torque or stirring power controlled by heating the temperature to 270 to 320°C while reducing the pressure from normal pressure to 200 15 Pa or lower. Further, the obtained polyester resin may be subjected to a solid-phase polymerization process and a vacuum reaction or nitrogen blowing at 200°C to a temperature lower than the melting point of the polyester resin as required to increase intrinsic 20 viscosity.

The antimony catalyst used in the present invention is generally used as a polycondensation catalyst and preferably added in the following manner. That is, diantimony trioxide may be used in powdery form 25 or may be dissolved or dispersed in glycols typified by ethylene glycol and then added. The catalyst may be added at any time before the start of the polycondensation reaction. It may be added in the initial or latter stage of the transesterification 30 reaction or esterification reaction or immediately before the start of the polycondensation reaction. (Fibers)

To form the obtained polyester into fibers, there is no need to employ a special method, and any known

melt-spinning method of polyester fibers can be employed under any conditions. For example, any fiber production method such as a method comprising melt-spinning the polyester at a rate of 500 to 2,500  
5 m/min and stretching and heat-treating the spun polyester, a method comprising melt-spinning the polyester at a rate of 1,500 to 5,000 m/min and carrying out stretching and tentative twisting simultaneously or successively or a method comprising melt-spinning  
10 the polyester at a high rate of not lower than 5,000 m/min and omitting a stretching step depending on applications is employed. A fiber to be spun by these methods may be a solid fiber free of a hollow portion or a hollow fiber having a hollow portion. Further,  
15 the external shape of the cross section of the polyester fiber to be spun and the shape of the hollow portion thereof may be circular or irregular. Further, the polyester fiber of the present invention can be preferably used as at least one component out of various  
20 polymers constituting a composite fiber.

The fiber of the present invention is particularly excellent in step conditions during high-speed spinning and stretchability and processability at the time of production thereof. As for the orientation  
25 crystallinity of produced fibers, the relationship between boiling water shrinkage (BWS) and birefringence ( $\Delta n$ ) preferably satisfies the following formula (1):

$$3,000 \times \Delta n \leq BWS \leq 5,000 \times \Delta n \quad (1)$$

When BWS is lower than  $3,000 \times \Delta n$ , it indicates  
30 that crystallinity has proceeded excessively, and fiber breakages during spinning, fiber breakages during stretching, lapping, non-uniform stretching and the like are liable to occur, thereby causing the occurrence of fuzz. Meanwhile, when BWS is higher than  $5,000 \times$

$\Delta n$ , the fiber tends to have poor strength since the fiber structure is not formed. The upper limit of BWS may be around  $4,000 \times \Delta n$  but is preferably  $5,000 \times \Delta n$ .

Fibers satisfying the above formula (1) can be  
5 produced by using the antimony catalyst of the present invention and using a polyester in which the amount of diethylene glycol copolymerized is 0.6 to 1.4 wt% based on the total weight of the polyester as described above.

## 10 Examples

Hereinafter, the present invention will be further described with reference to Examples. However, the present invention shall not be limited by these Examples in any way. Properties in Examples and  
15 Comparative Examples were measured in the following manner.

(1) Determination of Quantities of Diantimony Tetraoxide and Diantimony Pentaoxide: The antimony-derived peak of powder was measured for each  
20 crystal form by an X-ray diffractometer of Rigaku Corporation.

(2) Determination of Quantities of Pb, As and Fe elements in Diantimony Trioxide, Diantimony Tetraoxide and Diantimony Pentaoxide: After concentrated  
25 sulfuric acid was added to a sample which was then dissolved under heating, the resulting solution was adjusted to a constant volume by pure water, and the quantities of metal components were determined by use of ICPS-8100 of Shimadzu Corporation in accordance with  
30 an ICP fluorescence analysis (high-frequency plasma fluorescence analysis) method.

(3) Intrinsic Viscosity ( $[\eta]$ ): A sample was dissolved in a mixed solvent comprising 40 parts by weight of 1,1,2,2-tetrachlorethane and 60 parts by weight of

phenol, and the intrinsic viscosity thereof was measured at 35°C in the conventional manner.

(4) Quantity of Diethylene Glycol (DEG) Copolymerized: A sample and hydrazine hydrate were charged into an 5 eggplant-shaped flask equipped with a cooling pipe and then treated by a mantle heater for 2 hours. After completion of a decomposition reaction, the quantity of the obtained solution was determined by Shimadzu gas chromatograph GC-7G.

10 (5) Determination of Quantity of Antimony Compound in Polyester: A sample was measured for the quantity of an antimony element by use of the fluorescent X-ray model 3270 of Rigaku Corporation, and the measurement value was converted into the weight of diantimony 15 trioxide and taken as the content of an antimony compound.

20 (6) Color: A sample was measured for L, a and b by use of the color meter ZE-2000 of Nippon Denshoku Industries Co., Ltd., and the color of the sample was evaluated by the b value.

(7) Temperature Increasing Crystallization Temperature Tci, Temperature Decreasing Crystallization Temperature Tcd: DSC-7 of PerkinElmer Japan Co., Ltd. was used. After 10 mg of sample was 25 heated to 300°C at a rate of 20°C/min by DSC-7, it was quenched and then heated at a rate of 20°C/min again. The temperature of the peak top occurred was taken as Tci. After heated to 300°C, the sample was left to cool down. The temperature of the peak top of the 30 crystallization peak occurring during temperature decreasing was taken as Tcd.

(8) Semi-crystallization Time  $\tau$ : 1 g of sample was sandwiched between glass slides and kept on a hot plate at 285°C for 2 minutes. Then, the sample was quenched

to obtain a circular sheet-like sample. The sample was charged into a silicone oil bath having a visible light source and kept at 200°C, the attenuation of visible light transmittance due to whitening by crystallization 5 was recorded, and the half life was taken as  $\tau$ .

(9) Boiling Water Shrinkage (BWS): A fiber sample was placed in boiling water for 2 minutes, and the shrinkage thereof was measured.

(10) Birefringence ( $\Delta n$ ): A fiber sample was measured 10 by use of ECLIPSE E400 POL deflection microscope of Nikon Corporation.

(Reference Example 1)

• Preparation of Diantimony Trioxide (A1)

Diantimony trioxide (Pb content: 300 ppm, As 15 content: 300 ppm, Fe content: 5 ppm) of Nihon Mining & Concentrating Co., Ltd. was continuously molten at 700°C and fed to an oxidation tank, and hot air of the same temperature was fed into the tank at a rate of 2.4 m<sup>3</sup>/ton-Sb<sub>2</sub>O<sub>3</sub> to remove Pb. Then, after the resulting 20 diantimony trioxide was filtered, it was cooled down to the melting point and crystallized in 12 hours, thereby preparing diantimony trioxide (A1) having metal element contents shown in Table 1.

(Reference Example 2)

25 • Preparation of Diantimony Trioxide (A2)

Diantimony trioxide (A2) having metal element contents shown in Table 1 was prepared in the same manner as in Reference Example 1 except that diantimony trioxide (Pb content: 300 ppm, As content: 300 ppm, Fe 30 content: 300 ppm) of Mikuni Seiren Co., Ltd. was used and the feed rate of hot air was changed to 1.2 m<sup>3</sup>/ton-Sb<sub>2</sub>O<sub>3</sub> and the time for cooling down to the melting point and crystallization was changed to 6 hours to obtain metal element contents shown in Table 1.

## (Reference Example 3)

## • Preparation of Diantimony Trioxide (A3)

Diantimony trioxide (A3) having metal element contents shown in Table 1 was prepared in the same manner 5 as in Reference Example 1 except that diantimony trioxide of Mikuni Seiren Co., Ltd. used in Reference Example 2 was molten at 640°C, hot air of the same temperature was fed at a rate of 0.2 m<sup>3</sup>/ton-Sb<sub>2</sub>O<sub>4</sub> and the resulting compound was cooled down and crystallized 10 in 3 hours.

## (Reference Example 4)

## • Preparation of Diantimony Tetraoxide (B1)

Diantimony tetraoxide (Pb content: 500 ppm, As content: 500 ppm, Fe content: 10 ppm) of Mikuni Seiren 15 Co., Ltd. was continuously molten at 750°C, hot air of the same temperature was fed at a rate of 2 m<sup>3</sup>/ton-Sb<sub>2</sub>O<sub>4</sub>, and the resulting compound was cooled down and crystallized in 2 hours so as to prepare diantimony 20 tetraoxide (B1) having metal element contents shown in Table 1.

## (Reference Example 5)

## • Preparation of Diantimony Tetraoxide (B2)

Diantimony tetraoxide (Pb content: 500 ppm, As content: 500 ppm, Fe content: 10 ppm) of Mikuni Seiren 25 Co., Ltd. was continuously molten at 720°C, hot air of the same temperature was fed at a rate of 1 m<sup>3</sup>/ton-Sb<sub>2</sub>O<sub>4</sub>, and the resulting compound was cooled down and crystallized in 3 hours so as to prepare diantimony 30 tetraoxide (B2) having metal element contents shown in Table 1.

## (Reference Example 6)

## • Preparation of Diantimony Pentaoxide (C1)

Diantimony pentaoxide (Pb content: 400 ppm, As content: 400 ppm, Fe content: 10 ppm) of Nissan Chemical

Industries, Ltd. was continuously molten at 730°C, hot air of the same temperature was fed at a rate of 2 m<sup>3</sup>/ton-Sb<sub>2</sub>O<sub>5</sub>, and the resulting compound was cooled down and crystallized in 2 hours so as to prepare diantimony 5 pentaoxide (Cl) having metal element contents shown in Table 1.

(Example 1)

• Preparation of Antimony Catalyst Solution:

Diantimony trioxide (A1) and diantimony 10 tetraoxide (B1) were mixed together in the ratio shown in Table 2 to obtain a composition. The results of determination of the quantities of diantimony tetraoxide, Pb, As, and Fe in the composition are shown in Table 3. The obtained composition was dissolved in 15 ethylene glycol to a concentration of 1.3 wt% at 130°C for 2 hours so as to prepare an antimony catalyst solution.

• Production of Polyester:

A transesterification reaction was carried out in 20 the conventional manner by using 100 parts by weight of dimethyl terephthalate, 70 parts by weight of ethylene glycol and 0.5 parts by weight of diethylene glycol and using 0.038 parts by weight of manganese acetate tetrahydrate as a catalyst. After 0.025 parts 25 by weight of trimethyl phosphate was added to the produced oligomer and the mixture was allowed to react for 15 minutes, 2.3 parts by weight of the above antimony catalyst solution was added. Further, ethylene glycol which contained titanium dioxide was also added such 30 that the content of titanium dioxide was 0.3 wt% based on a titanium dioxide containing polyester. Then, the internal temperature was increased from 250°C to 290°C, and a polycondensation reaction was carried out under a reduced pressure of 0.133 kPa or lower for 3 hours

so as to obtain a polyester having a  $[\eta]$  of 0.62 dL/g. The content of an antimony compound in the obtained polyester was 0.031 wt%. The measurement results of the properties of the polyester are shown in Table 4.

5 · Production of Polyester Fibers:

The obtained polyester was discharged from a spinneret having 24 openings at 295°C and taken up directly at a spinning rate of 5,000 m/min. The polymer discharge rate was adjusted such that the total fiber 10 fineness of the taken-up fibers was 150 dtex. Fiber production was conducted for 3 days, and the number of fiber breakages during spinning was counted. The intrinsic viscosity of this polyester fiber was 0.60 dL/g. The evaluation results of the polyester fibers 15 are shown in Table 5.

(Examples 2 and 3 and Comparative Examples 1 and 2)

· Preparation of Antimony Catalyst Solution:

The procedure of Example 1 was repeated except that the composition of the antimony catalyst was 20 changed as shown in Table 2. The results of determination of the quantities of diantimony tetraoxide, diantimony pentaoxide, Pb, As, and Fe in the catalyst compositions are shown in Table 3.

· Production of Polyester:

25 The procedure of Example 1 was repeated except that the amount of diethylene glycol (DEG) to be added was changed as appropriate such that the amount of diethylene glycol copolymerized became as shown in Table 4. The contents of antimony compounds in the 30 polyesters obtained in Example 2 and Comparative Example 1 were 0.031 wt% as in Example 1. The contents of antimony compounds in Example 3 and Comparative Example 2 were 0.030 wt% and 0.032 wt%, respectively. The measurement results of the properties of the

polyesters are shown in Table 4.

• Production of Polyester Fibers:

Polyester fibers were produced in the same manner as in Example 1. The results are shown in Table 5.

5 (Comparative Example 3)

• Preparation of Antimony Catalyst Solution:

The procedure of Example 1 was repeated except that the composition of the antimony catalyst was changed as shown in Table 2. The results of 10 determination of the quantities of diantimony tetraoxide, Pb, As, and Fe in the catalyst composition are shown in Table 3.

• Production of Polyester:

The procedure of Example 1 was repeated except 15 that diethylene glycol was not added. The content of an antimony compound in the obtained polyester was 0.031 wt% as in Example 1. The results are shown in Table 4.

• Production of Polyester Fibers:

20 Polyester fibers were produced in the same manner as in Example 1. The results are shown in Table 5.  
(Example 4)

• Preparation of Antimony Catalyst Solution:

The procedure of Example 1 was repeated to prepare 25 an antimony catalyst. The results of determination of the quantities of diantimony tetraoxide, Pb, As, and Fe in the catalyst composition are shown in Table 3.

• Production of Polyester:

The procedure of Example 1 was repeated except 30 that the amount of diethylene glycol (DEG) to be added was changed such that the amount of DEG copolymerized became as shown in Table 4 and the antimony catalyst solution was added in an amount of 1.53 parts by weight. The content of an antimony compound in the obtained

polyester was 0.020 wt%. The measurement results of the properties of the polyester are shown in Table 4.

• Production of Polyester Fibers:

Polyester fibers were produced in the same manner 5 as in Example 1. The results are shown in Table 5.  
(Example 5)

• Preparation of Antimony Catalyst Solution:

The procedure of Example 1 was repeated to prepare 10 an antimony catalyst. The results of determination of the quantities of diantimony tetraoxide, Pb, As, and Fe in the catalyst composition are shown in Table 3.

• Production of Polyester:

The procedure of Example 1 was repeated except 15 that the amount of diethylene glycol (DEG) to be added was changed such that the amount of DEG copolymerized became as shown in Table 4 and the antimony catalyst solution was added in an amount of 3.45 parts by weight. The content of an antimony compound in the obtained 20 polyester was 0.046 wt%. The measurement results of the properties of the polyester are shown in Table 4.

• Production of Polyester Fibers:

Polyester fibers were produced in the same manner 25 as in Example 1. The results are shown in Table 5.  
(Example 6)

• Preparation of Antimony Catalyst Solution:

The procedure of Example 1 was repeated to prepare 30 an antimony catalyst. The results of determination of the quantities of diantimony tetraoxide, Pb, As, and Fe in the catalyst composition are shown in Table 3.

• Production of Polyester:

The procedure of Example 1 was repeated except that the amount of diethylene glycol (DEG) to be added was changed such that the amount of DEG copolymerized became as shown in Table 4 and the antimony catalyst

solution was added in an amount of 4.6 parts by weight. The content of an antimony compound in the obtained polyester was 0.061 wt%. The measurement results of the properties of the polyester are shown in Table 4.

5 · Production of Polyester Fibers:

Polyester fibers were produced in the same manner as in Example 1. The results are shown in Table 5. (Examples 7, 8 and 9)

· Preparation of Antimony Catalyst Solution:

10 The procedure of Example 1 was repeated except that the composition of the antimony catalyst was changed as shown in Table 2. The results of determination of the quantities of diantimony tetraoxide, diantimony pentaoxide, Pb, As, and Fe in 15 the catalyst compositions are shown in Table 3.

· Production of Polyester:

The procedure of Example 1 was repeated except that the amount of diethylene glycol (DEG) to be added was changed as appropriate such that the amount of 20 diethylene glycol copolymerized became as shown in Table 4. The contents of antimony compounds in the obtained polyesters were 0.030 wt%. The measurement results of the properties of the polyesters are shown in Table 4.

25 · Production of Polyester Fibers:

Polyester fibers were produced in the same manner as in Example 1. The results are shown in Table 5. (Example 10)

· Preparation of Antimony Catalyst Solution:

30 Diantimony trioxide (A1) and diantimony tetraoxide (B1) were mixed together in the ratio shown in Table 2 to obtain a composition. The results of determination of the quantities of diantimony tetraoxide, diantimony pentaoxide, Pb, As, and Fe in

the composition are shown in Table 3. The obtained composition was dissolved in ethylene glycol to a concentration of 1.3 wt% at 130°C for 2 hours so as to prepare an antimony catalyst solution.

5 • Production of Polyester:

An esterification reaction was carried out in the conventional manner by using 85.5 parts by weight of terephthalic acid and 70 parts by weight of ethylene glycol in the absence of a catalyst under an increased 10 pressure of 0.3 MPa at 255°C. To the produced oligomer, 85.5 parts by weight of terephthalic acid and 70 parts by weight of ethylene glycol were further added, and an esterification reaction was carried out in the conventional manner under an increased pressure of 0.1 15 MPa at 255°C. A 1/2 volume of the produced oligomer was collected, and an esterification reaction was carried out in an esterification reaction tank in the conventional manner by use of 85.5 parts by weight of terephthalic acid and 70 parts by weight of ethylene 20 glycol under an increased pressure of 0.1 MPa at 255°C. This operation was repeated five times. Then, after 0.025 parts by weight of trimethyl phosphate was added to a collected 1/2-volume oligomer and allowed to react 25 for 15 minutes, 2.3 parts by weight of the above antimony catalyst solution was added. Further, ethylene glycol which contained titanium dioxide was added such that the content of titanium dioxide was 0.3 wt% based on a polyester containing titanium dioxide to be obtained. Then, the internal temperature was increased from 250°C 30 to 290°C, and a polycondensation reaction was carried out under a reduced pressure of 0.133 kPa or lower for 3 hours so as to obtain a polyester having a  $[\eta]$  of 0.62 dL/g. The content of an antimony compound in the obtained polyester was 0.031 wt%. The measurement

results of the properties of the polyester are shown in Table 4.

• Production of Polyester Fibers:

The obtained polyester was discharged from a spinneret having 24 openings at 295°C and taken up directly at a spinning rate of 5,000 m/min. The polymer discharge rate was adjusted such that the total fiber fineness of the taken-up fibers was 150 dtex. Fiber production was conducted for 3 days, and the number of fiber breakages during spinning was counted. The intrinsic viscosity of this polyester fiber was 0.59 dL/g. The evaluation results of the polyester fibers are shown in Table 5.

(Comparative Example 4)

• Production of Polyester:

An transesterification reaction was carried out in the conventional manner by using 100 parts by weight of dimethyl terephthalate, 70 parts by weight of ethylene glycol and 0.5 parts by weight of diethylene glycol and using 5.36 parts by weight of 1-wt% ethylene glycol solution of tetrabutyl titanium as a catalyst. 0.025 parts by weight of trimethyl phosphate was added to the produced oligomer and allowed to react for 15 minutes. Then, ethylene glycol which contained titanium dioxide was added such that the content of titanium dioxide was 0.3 wt% based on a polyester containing titanium dioxide. Thereafter, the internal temperature was increased from 250°C to 290°C, and a polycondensation reaction was carried out under a reduced pressure of 0.133 kPa or lower for 3 hours so as to obtain a polyester having a  $[\eta]$  of 0.64 dL/g. The content of an antimony compound in the obtained polyester was 0.0 wt%. The measurement results of the properties of the polyester are shown in Table 4.

• **Production of Polyester Fibers:**

The obtained polyester was discharged from a spinneret having 24 openings at 295°C and taken up directly at a spinning rate of 5,000 m/min. The polymer discharge rate was adjusted such that the total fiber fineness of the taken-up fibers was 150 dtex. Fiber production was conducted for 3 days, and the number of fiber breakages during spinning was counted. The intrinsic viscosity of this polyester fiber was 0.60 dL/g. The evaluation results of the polyester fibers are shown in Table 5.

**Industrial Applicability**

According to the present invention, there is provided a polyester whose crystallization rate is controlled during high-speed spinning. Since the polyester of the present invention is less liable to crystallize during high-speed spinning than conventional polyesters, subsequent stretching and twisting operations can be performed easily. Thus, productivity of twisted polyester fibers can be increased.

Table 1

|        | Type of Antimony      | Symbol | Metal Element Content (weight ppm) |     |     |
|--------|-----------------------|--------|------------------------------------|-----|-----|
|        |                       |        | Pb                                 | As  | Fe  |
| R.Ex.1 | Diantimony Trioxide   | A1     | 20                                 | 20  | 0   |
| R.Ex.2 | Diantimony Trioxide   | A2     | 150                                | 100 | 40  |
| R.Ex.3 | Diantimony Trioxide   | A3     | 200                                | 200 | 100 |
| R.Ex.4 | Diantimony Tetraoxide | B1     | 30                                 | 20  | 0   |
| R.Ex.5 | Diantimony Tetraoxide | B2     | 70                                 | 80  | 5   |
| R.Ex.6 | Diantimony Pentaoxide | C1     | 60                                 | 60  | 0   |

R.Ex. : Reference Example

Table 2

|          |        | Amount of Antimony Catalyst |                       |                       |
|----------|--------|-----------------------------|-----------------------|-----------------------|
|          |        | Diantimony Trioxide         | Diantimony Tetraoxide | Diantimony Pentaoxide |
|          |        | Type/Parts by Weight        | Type/Parts by Weight  | Type/Parts by Weight  |
| Ex. 1    | A1/100 |                             | B1/1                  | 0                     |
| Ex. 2    | A1/100 | 0                           |                       | C1/1                  |
| Ex. 3    | A1/100 |                             | B1/1                  | C1/1                  |
| C. Ex. 1 | A3/100 | 0                           |                       | 0                     |
| C. Ex. 2 | A1/100 |                             | B2/30                 | C1/30                 |
| C. Ex. 3 | A2/100 |                             | B2/15                 | 0                     |
| Ex. 4    | A1/100 |                             | B1/1                  | 0                     |
| Ex. 5    | A1/100 |                             | B1/1                  | 0                     |
| Ex. 6    | A1/100 |                             | B1/1                  | 0                     |
| Ex. 7    | A1/100 |                             | B1/5                  | 0                     |
| Ex. 8    | A1/100 | 0                           |                       | C1/5                  |
| Ex. 9    | A1/100 |                             | B1/4                  | C1/4                  |
| Ex. 10   | A1/100 |                             | B1/1                  | 0                     |
| C. Ex. 4 | -      |                             | -                     | -                     |

Ex. : Example, C.Ex. : Comparative Example

Table 3

| Composition of Antimony Catalyst |                        |                          |                          |               |               |               | Fe            |
|----------------------------------|------------------------|--------------------------|--------------------------|---------------|---------------|---------------|---------------|
|                                  | Diantimony<br>Trioxide | Diantimony<br>Tetraoxide | Diantimony<br>Pentaoxide | Pb            | As            |               |               |
|                                  | wt%                    | wt%                      | wt%                      | weight<br>ppm | weight<br>ppm | weight<br>ppm | weight<br>ppm |
| Ex. 1                            | 99.0                   | 1.0                      | 0                        | 20            | 20            | 0             | 0             |
| Ex. 2                            | 99.0                   | 0                        | 1.0                      | 21            | 20            | 0             | 0             |
| Ex. 3                            | 98.0                   | 1.0                      | 1.0                      | 21            | 21            | 0             | 0             |
| C.Ex. 1                          | 100                    | 0                        | 0                        | 200           | 200           | 100           | 100           |
| C.Ex. 2                          | 62.5                   | 18.8                     | 18.8                     | 37            | 39            | 1             | 1             |
| C.Ex. 3                          | 87.0                   | 13.0                     | 0                        | 140           | 97            | 35            | 35            |
| Ex. 4                            | 99.0                   | 1                        | 0                        | 20            | 19            | 0             | 0             |
| Ex. 5                            | 99.0                   | 1                        | 0                        | 19            | 20            | 0             | 0             |
| Ex. 6                            | 99.0                   | 1                        | 0                        | 20            | 20            | 0             | 0             |
| Ex. 7                            | 99.0                   | 1                        | 0                        | 20            | 20            | 0             | 0             |
| Ex. 8                            | 95.2                   | 0                        | 4.75                     | 20            | 22            | 0             | 0             |
| Ex. 9                            | 92.6                   | 3.7                      | 3.7                      | 22            | 21            | 0             | 0             |
| Ex. 10                           | 99.0                   | 1.0                      | 0                        | 20            | 20            | 0             | 0             |
| C.Ex. 4                          | 0                      | 0                        | 0                        | 0             | 0             | 0             | 0             |

Ex.: Example, C.Ex.: Comparative Example

Table 4

| Properties of Polyester |                                |       |                 |                 |                     |         |
|-------------------------|--------------------------------|-------|-----------------|-----------------|---------------------|---------|
| [ $\eta$ ]              | Amount of DEG<br>Copolymerized | Col-b | T <sub>c1</sub> | T <sub>cd</sub> | T <sub>cd-Tc1</sub> | $\tau$  |
| dL/g                    | wt%                            |       | °C              | °C              | °C                  | seconds |
| Ex.1                    | 0.62                           | 1.20  | 6.2             | 170             | 192                 | 22      |
| Ex.2                    | 0.62                           | 1.18  | 6.2             | 168             | 188                 | 20      |
| Ex.3                    | 0.62                           | 1.15  | 6.2             | 169             | 190                 | 21      |
| C.Ex.1                  | 0.62                           | 1.15  | 8.5             | 155             | 206                 | 51      |
| C.Ex.2                  | 0.59                           | 1.08  | 10.2            | 169             | 204                 | 35      |
| C.Ex.3                  | 0.62                           | 0.45  | 8.0             | 156             | 205                 | 49      |
| Ex.4                    | 0.62                           | 1.17  | 6.4             | 170             | 192                 | 22      |
| Ex.5                    | 0.63                           | 1.14  | 5.9             | 168             | 192                 | 24      |
| Ex.6                    | 0.64                           | 1.10  | 5.7             | 168             | 193                 | 25      |
| Ex.7                    | 0.62                           | 1.16  | 6.5             | 165             | 194                 | 29      |
| Ex.8                    | 0.61                           | 1.18  | 6.7             | 163             | 193                 | 30      |
| Ex.9                    | 0.62                           | 1.20  | 6.9             | 164             | 195                 | 31      |
| Ex.10                   | 0.63                           | 1.20  | 6.8             | 170             | 194                 | 24      |
| C.Ex.4                  | 0.64                           | 1.18  | 12.4            | 158             | 201                 | 43      |
|                         |                                |       |                 |                 |                     | 18      |

Ex. : Example, C.Ex. : Comparative Example

Table 5

| Evaluation of Polyester Fibers |                            |                    |            |          |
|--------------------------------|----------------------------|--------------------|------------|----------|
|                                | Number of Fiber Breakages  | [ $\eta$ ]<br>dL/g | $\Delta n$ | BWS<br>% |
| Ex.1                           | 0                          | 0.60               | 0.012      | 53       |
| Ex.2                           | 0                          | 0.61               | 0.013      | 49       |
| Ex.3                           | 0                          | 0.61               | 0.011      | 48       |
| C.Ex.1                         | 1                          | 0.60               | 0.015      | 40       |
| C.Ex.2                         | >10, Impossible<br>to Spin | -                  | -          | -        |
| C.Ex.3                         | 3                          | 0.60               | 0.013      | 35       |
| Ex.4                           | 0                          | 0.60               | 0.012      | 53       |
| Ex.5                           | 0                          | 0.60               | 0.013      | 50       |
| Ex.6                           | 0                          | 0.61               | 0.012      | 49       |
| Ex.7                           | 0                          | 0.60               | 0.012      | 49       |
| Ex.8                           | 0                          | 0.61               | 0.013      | 48       |
| Ex.9                           | 1                          | 0.61               | 0.013      | 47       |
| Ex.10                          | 0                          | 0.60               | 0.013      | 53       |
| C.Ex.4                         | 2                          | 0.58               | 0.020      | 35       |

Ex.: Example, C.Ex.: Comparative Example